



## **Sr-Nd-Hf Isotopic Analysis of <10 mg Dust Samples: Implications for Ice Core Dust Source Fingerprinting**

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## RESEARCH ARTICLE

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## Key Points:

- Combined Sr-Nd-Hf isotopic ratios were obtained from small size (5–10 mg) dust samples
- European/North American dusts have less radiogenic Hf isotopic signatures than those of SE Asian dust
- Modeling suggests that  $\epsilon\text{Hf}(0)$  of the  $<2\ \mu\text{m}$  fraction of dust is negligibly affected by zircons and may distinguish between dust sources

## Supporting Information:

- Supporting Information S1
- Figure S1
- Figure S2
- Figure S3
- Figure S4
- Table S1
- Table S2
- Table S3
- Data Set S1

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Sr-Nd-Hf Isotopic Analysis of  $<10\ \text{mg}$  Dust Samples: Implications for Ice Core Dust Source Fingerprinting

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**Abstract** Combined Sr-Nd-Hf isotopic data of two reference materials (AGV-1/BCR2) and 50, 10, and 5 mg aliquots of carbonate-free fine grain ( $<10\ \mu\text{m}$ ) separates of three loess samples (Central Europe/NUS, China/BEI, USA/JUD) are presented. Good agreement between measured and reference Sr-Nd-Hf isotopic compositions (ICs) demonstrate that robust isotopic ratios can be obtained from 5 to 10 mg size rock samples using the ion exchange/mass spectrometry techniques applied. While  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of dust aluminosilicate fractions are affected by even small changes in pretreatments, Nd isotopic ratios are found to be insensitive to acid leaching, grain-size or weathering effects. However, the Nd isotopic tracer is sometimes inconclusive in dust source fingerprinting (BEI and NUS both close to  $\epsilon\text{Nd}(0) -10$ ). Hafnium isotopic values ( $<10\ \mu\text{m}$  fractions) are homogenous for NUS, while highly variable for BEI. This heterogeneity and vertical arrays of Hf isotopic data suggest zircon depletion effects toward the clay fractions ( $<2\ \mu\text{m}$ ). Monte Carlo simulations demonstrate that the Hf IC of the dust  $<10\ \mu\text{m}$  fraction is influenced by both the abundance of zircons present and maturity of crustal rocks supplying this heavy mineral, while the  $<2\ \mu\text{m}$  fraction is almost unaffected. Thus,  $\epsilon\text{Hf}(0)$  variations in the clay fraction are largely controlled by the Hf IC of clays/heavy minerals having high Lu/Hf and radiogenic  $^{176}\text{Hf}/^{177}\text{Hf}$  IC. Future work should be focused on Hf IC of both the  $<10$  and  $<2\ \mu\text{m}$  fractions of dust from potential source areas to gain more insight into the origin of last glacial dust in Greenland ice cores.

## 1. Introduction

Eolian mineral dust particles less than 10–20  $\mu\text{m}$  in size can be transported vast distances before deposition (Shao, 2008). This transport can occur on intercontinental scales (Arimoto et al., 1997; Prospero & Lamb, 2003), such that eolian dust is a useful tracer of large-scale atmospheric circulation at various times in Earth history. Satellite imagery, back-trajectory analysis, and chemical transport models coupled with ground-based measurements are commonly employed to identify the sources of dust in modern dust plumes (Shao et al., 2011). To identify dust sources in past archives such as deep-sea sediments, lacustrine/loess deposits, or ice cores, the mineralogy and geochemistry of the wind-blown dust must be documented (Biscaye, 1965; Biscaye et al., 1997; Grousset et al., 1988; Scheuven et al., 2013). While the amount of dust in marine cores or common terrestrial records is usually adequate in some sedimentary horizons for different types of analyses and even for multiple repeat measurements, the overall dust content in ice cores is usually extremely low even for the peak dusty periods such as the Last Glacial Maximum (LGM) (5–8 mg dust/kg ice; Ruth et al., 2003). Since the most powerful dust fingerprinting methods, such as REE composition (Ferrat et al., 2011; Gallet et al., 1998; Zdanowicz et al., 2006) and Sr-Nd-Pb isotopic analyses (e.g., Grousset & Biscaye, 2005), are destructive, there is a clear need to establish sequential separation techniques of Sr, Nd, Pb and other REEs to retrieve the most information from small (5–10 mg) dust samples recovered from ice cores. Although Hf isotopes have recently been added as a tool of aerosol/dust source discrimination (Aarons et al., 2013; Aciego et al., 2009; Blakowski et al., 2016; Lupker et al., 2010; Pettke et al., 2002; Pourmand et al., 2014; Újvári et al., 2015; Zhao et al., 2014, 2015), precise Hf isotopic measurements of small ( $<10\ \text{mg}$ ) dust samples are still challenging due to their minute amounts of Hf (on the order of 1–10 ng); these analyses are often compromised by problems that can arise during ion exchange chemistry. Such problems may include high Lu and Yb blanks causing inaccurate interference corrections on  $^{176}\text{Hf}$  (Münker et al., 2001),

insufficient Ti removal leading to reduced Hf transmission in the mass spectrometer (Blichert-Toft et al., 1997; Wimpenny et al., 2013), and high Zr/Hf producing bias on  $^{176}\text{Hf}/^{177}\text{Hf}$  ratios (Peters et al., 2015).

In this study we adopted an improved method for chemical separation of Sr, Nd and Hf recently developed by Bast et al. (2015) following classical procedures reported by Patchett and Tatsumoto (1980), Münker et al. (2001) and Wimpenny et al. (2013), which allows the precise isotope analysis of sub-ng amounts of Hf by MC-ICPMS. This ion exchange chromatography technique was combined with methods of separating and purifying Sr and Nd for subsequent TIMS isotopic measurements. International rock reference materials AGV-1 and BCR-2 (10 mg aliquots) were used to demonstrate that the experimental setup allow for valid  $^{176}\text{Lu}$  and  $^{176}\text{Yb}$  corrections, and in turn results in reliable  $^{176}\text{Hf}/^{177}\text{Hf}$  (and also  $^{87}\text{Sr}/^{86}\text{Sr}$ ,  $^{143}\text{Nd}/^{144}\text{Nd}$ ) ratios. Along with the standards 50, 10, and 5 mg aliquots of the fine ( $<10\ \mu\text{m}$ ) fractions of three wind-blown loess sediment samples from Central Europe, China and the US were processed to (1) demonstrate that reproducible Sr, Nd and Hf isotopic ratios can be obtained from small size ( $<10\ \text{mg}$ ) dust samples with the applied procedure by comparing these ratios to those acquired on larger samples (Újvári et al., 2015), (2) to reveal intra- and inter-sample variabilities in isotopic signatures, (3) to test acid pretreatment effects on the isotopic ratios, and (4) to gain insight into the uncertainties of Hf isotopic ratios of small volume dust samples and their suitability for distinguishing dust sources. Furthermore, Monte Carlo simulations were performed to model zircon depletion effects for two grain size fractions ( $<10$  and  $<2\ \mu\text{m}$ ) of a hypothetical 5 mg dust sample. This provides unique insight into the major controlling factors of fine dust Hf isotopic compositions and general applicability of the Hf isotope tracer to distinguish dust source areas.

## 2. Materials and Methods

### 2.1. Samples and Preparation

Two rock reference materials and three loess samples were analyzed in this study. Both the AGV-1 granite and the USGS reference material BCR-2 (Columbia River Basalt 2) were used as chemical processing and instrumental quality control monitors for isotopic measurements. Powdered reference samples (10 mg each) were digested without any pretreatment for subsequent elemental separations.

The loess sediment samples were collected at the Nussloch site in Germany ( $49^{\circ}18'59''\text{N}$ ,  $8^{\circ}43'54''\text{E}$ ) (Gocke et al., 2014; Rousseau et al., 2002), the Beigoyuan site in China ( $36^{\circ}37'36''\text{N}$ ,  $107^{\circ}16'57''\text{E}$ ) (Stevens et al., 2008), and the Judkins site in Nebraska, USA ( $41^{\circ}29'\text{N}$ ,  $100^{\circ}11'\text{W}$ ) (Sweeney & Mason, 2013). After collection, the loess samples were dried at room temperature and the  $<10\ \mu\text{m}$  particle size fraction was isolated by wet sedimentation (Stokes Law). Subsequently, 0.5 mol/L acetic acid was added at room temperature to each fine particle sample to remove carbonates as done for dust samples from the GRIP ice core (Svensson et al., 2000). Following the dissolution of carbonates within the fine particle sample (ca. 1–1.5 h), the remaining acid was washed away using ultrapure water. After intense stirring, the samples were allowed to settle and the remaining liquid was decanted by syringe after 55–57 min, and dried on a hotplate at  $50^{\circ}\text{C}$  leaving the fine particles behind. Grain size distributions of these fine separates are dominated by 1–10  $\mu\text{m}$  particles with peaks at 3–4  $\mu\text{m}$  (see supporting information in Újvári et al., 2015). To investigate the effects of different acid treatments on measured isotopic ratios, the sample size was reduced ( $\sim 20\ \text{g}$ ) and various sample-to-acid ratios were employed. This different sample treatment was then compared to the scheme outlined in Újvári et al. (2015), which used larger samples (150–200 g) for the acid dissolution.

### 2.2. Column Chemistry

All the analytical work was performed in class 100 clean laboratory at the Department of Lithospheric Research, University of Vienna. Details on Sr-Nd-Hf separations can be found in supporting information Text S1, Figure S1, and Tables S1 and S2.

### 2.3. Mass Spectrometry

#### 2.3.1. TIMS Measurements

Sr and Nd isotopic analyses were performed at the Department of Lithospheric Research, University of Vienna using a Thermo-Finnigan Triton TI multi-collector TIMS instrument in static mode. The pure element fractions were analyzed using a Re double filament assembly with currents on the ionization and evaporation filaments of  $\sim 2,500$  (Sr)/ $\sim 4,500$  (Nd) and 350–800 (Sr)/900–1,200 (Nd) mA. Measurements were done at ca 7V (Sr) and 1–2V (Nd). The on-peak integration time was 8 seconds, while the idle time was set to 3

**Table 1**  
Faraday Cup Configurations for Hf Isotopic Measurements Using Nu Plasma II MC-ICPMS

Cups	H6	H7	H8	H9	H10	H11	H12	H14
Isotopes	<sup>180</sup> Hf	<sup>179</sup> Hf	<sup>178</sup> Hf	<sup>177</sup> Hf	<sup>176</sup> (Hf+Lu+Yb)		<sup>174</sup> Hf	
						<sup>175</sup> Lu		<sup>172</sup> Yb

seconds. Ten cycles were collected into 1 block and 80 blocks were measured to obtain the isotopic ratios. A mean <sup>87</sup>Sr/<sup>86</sup>Sr ratio of  $0.710281 \pm 0.000004$  ( $n = 15$ ; error is  $2\sigma$  of the mean) was determined for the international standard NBS987 (ref. value: <sup>87</sup>Sr/<sup>86</sup>Sr = 0.710248; Faure, 2001) and a mean <sup>143</sup>Nd/<sup>144</sup>Nd ratio of  $0.511846 \pm 0.000004$  ( $n = 6$ ) for the La Jolla (ref. value: <sup>143</sup>Nd/<sup>144</sup>Nd = 0.511858; Lugmair & Carlson, 1978) international standards during the analysis periods. Mass fractionation during measurement was corrected for <sup>86</sup>Sr/<sup>88</sup>Sr = 0.1194, and <sup>146</sup>Nd/<sup>144</sup>Nd = 0.7219, respectively. Uncertainties of isotopic ratios represent  $2\sigma$  errors of the mean. Neodymium (<sup>143</sup>Nd/<sup>144</sup>Nd) isotopic ratios are also reported as  $\epsilon\text{Nd}(0) = ((^{143}\text{Nd}/^{144}\text{Nd}_{\text{sample}}/^{143}\text{Nd}/^{144}\text{Nd}_{\text{CHUR}}) - 1) \times 10^4$  in this study using the present-day chondritic uniform reservoir (CHUR) value of  $0.512630 \pm 0.000011$  (Bouvier et al., 2008). Uncertainties of  $\epsilon\text{Nd}(0)$  values were propagated as  $\sqrt{((\partial\epsilon/\partial x)\sigma_x)^2 + ((\partial\epsilon/\partial y)\sigma_y)^2} = \sqrt{((1/y)10000\sigma_x)^2 + ((-x/y^2)10000\sigma_y)^2}$ , where  $\epsilon = \epsilon\text{Nd}(0)$ ,  $x = ^{143}\text{Nd}/^{144}\text{Nd}_{\text{sample}}$ ,  $y = ^{143}\text{Nd}/^{144}\text{Nd}_{\text{CHUR}}$ ,  $\sigma_x$  and  $\sigma_y$  are uncertainties of  $x$  and  $y$ .

### 2.3.2. MC-ICPMS Analysis

Hafnium isotope analyses were performed at the NAWI Central Laboratory for Water, Minerals and Rocks, a joint lab facility of Karl-Franzens-University and Graz University of Technology (GUT). Dried samples (from column #5; supporting information Figure S1) were dissolved in 0.1 mL 0.1 M HNO<sub>3</sub> overnight and diluted to a sample volume of 2 mL prior to analysis for appropriate concentrations and ~15 min. analysis time. A Nu Instruments DSN100 desolvating nebulizer system equipped with a MicroMist glass nebulizer with a flow rate of 100 mL/min was used as the sample introduction system. All standards and samples were analyzed during one single analytical session and a Faraday gain calibration occurred prior to standard and sample measurements.

Hafnium isotope analyses were performed in dry-plasma mode on a Nu Plasma II MC-ICPMS. A wash out cycle 10 min in duration of 1 M HNO<sub>3</sub> occurred between individual measurements. The overall sensitivity for Hf was between 420 V/ppm and 140 V/ppm Hf. Hafnium isotopes (<sup>174</sup>Hf, <sup>176</sup>Hf, <sup>177</sup>Hf, <sup>178</sup>Hf, <sup>179</sup>Hf, and <sup>180</sup>Hf) and one of each interfering element (<sup>182</sup>W, <sup>172</sup>Yb, <sup>175</sup>Lu) were measured simultaneously using the Faraday cup configuration shown in Table 1. Analyses comprised 20 blocks each with 5 cycles with an integration time of 8 sec. Baselines were measured at mid-masses at the beginning of each cycle for 5 sec.

An exponential mass bias correction  $\beta\text{Hf}$  is applied using <sup>179</sup>Hf/<sup>177</sup>Hf = 0.7325 (Griffin et al., 2006). <sup>176</sup>Lu and <sup>176</sup>Yb interference corrections on <sup>176</sup>Hf were made using the recommended values of Griffin et al. (2006) (<sup>176</sup>Lu/<sup>175</sup>Lu = 0.02653 and <sup>176</sup>Yb/<sup>172</sup>Yb = 0.5870). Mass bias factors  $\beta\text{Yb}$  and  $\beta\text{Lu}$  were calculated from  $\beta\text{Hf}$ . All reported errors are 2 standard errors of the mean, unless stated otherwise.

The <sup>176</sup>Hf/<sup>177</sup>Hf isotopic composition of JMC-475 standard was  $0.282142 \pm 0.000001$  and  $0.282146 \pm 0.000001$  for the 100 ppb,  $0.282156 \pm 0.000005$  and  $0.282159 \pm 0.000005$  for the 10 ppb, as well as  $0.282248 \pm 0.000003$  and  $0.282227 \pm 0.000003$  for the 1 ppb concentration solutions versus the accepted value of  $0.282159 \pm 0.000038$  (Chu et al., 2002). Calculated Hf concentrations in the rock standard and loess sample solutions varied between 1 and 21.4 ppb (mean: 7 ppb), coinciding with the 10 ppb JMC-475 Hf standard solution. Since the measured Hf isotopic ratios of JMC-475 (100 and 10 ppb) were within a few ppm of the reference values the <sup>176</sup>Hf/<sup>177</sup>Hf isotopic ratios were not normalized to a <sup>176</sup>Hf/<sup>177</sup>Hf of 0.282160 for JMC-475. Such a normalization would insignificantly affect the reported Hf isotopic data and its omission does not compromise data comparison.  $\epsilon\text{Hf}(0)$  values and associated uncertainties were calculated as given for Nd, but using a present-day chondritic uniform reservoir (CHUR) value of <sup>176</sup>Hf/<sup>177</sup>Hf<sub>CHUR</sub> =  $0.282785 \pm 0.000011$  (Bouvier et al., 2008).

### 2.4. Monte Carlo (MC) Simulations

MC simulations were performed for two particle size fractions (<10 and <2 μm) of a hypothetical 5 mg dust sample using MATLAB (release 2008b) and involved 1,000 iterations. Details of the zircon depletion

model, probability distributions used in simulations (zircon abundances in each size fractions, Hf contents and isotopic compositions) and sensitivity tests performed are given in the supporting information (SI Text 2, Figure S2-4, and Table S3). Zircons are assumed to be originated from hinterlands assembled from Archean/Proterozoic and Phanerozoic rocks (average crust,  $\epsilon\text{Hf}(0)_{\text{zircon}}: -20 \pm 10$ ), but further tests were performed with supposed Archean and Phanerozoic crusts ( $\epsilon\text{Hf}(0)_{\text{zircon}}: -40 \pm 10$  and  $-10 \pm 10$ ), respectively.

### 3. Results

#### 3.1. Isotopic Compositions of International Rock Reference Materials

The  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $^{143}\text{Nd}/^{144}\text{Nd}$  isotope compositions of the 10 mg AGV-1 granite standard were  $0.704088 \pm 0.000003$  and  $0.512775 \pm 0.000003$  (Table 2), overlapping with the certified values of  $0.704036 \pm 0.000155$  and  $0.512780 \pm 0.000022$  (Jochum et al., 2005). The 10 mg BCR-2 standard samples yielded slightly more radiogenic Sr isotopic ratios ( $0.705127 \pm 0.000004$ , repeat:  $0.705139 \pm 0.000004$ ) than the accepted value of  $0.705000 \pm 0.000011$  (Jweda et al., 2016). The Nd isotopic ratios of BCR-2 were  $0.512625 \pm 0.000004$  and  $0.512622 \pm 0.000003$  (repeat) matching very well the reference value of  $0.512637 \pm 0.000013$  (Jweda et al., 2016). The  $^{176}\text{Hf}/^{177}\text{Hf}$  isotope composition of the 10 mg AGV-1 granite was less radiogenic ( $0.282892 \pm 0.000010$ ) than the certified value ( $0.282978 \pm 0.000011$ ; Jochum et al., 2005). At the same time, the 10 mg BCR-2 basalt samples yielded Hf isotopic ratios of  $0.282853 \pm 0.000006$  and  $0.282859 \pm 0.000008$ , being in extremely good agreement with the accepted value of  $0.282866 \pm 0.000011$  (Jweda et al., 2016). These isotopic data demonstrate that the column chemistry and mass spectrometry procedures described above provide valid Sr-Nd-Hf isotopic ratios from reference rock samples as small as 10 mg.

#### 3.2. Isotopic Compositions of Loess Fine Grain (<10 Mm) Separates

Strontium isotopic compositions of the 50, 10, and 5 mg aliquots of BEI and NUS are in a relatively narrow range ( $\Delta^{87}\text{Sr}/^{86}\text{Sr} = 0.000072$  for BEI and  $0.000408$  for NUS, excluding NUS-AA2-M3-10 mg, where  $\Delta^{87}\text{Sr}/^{86}\text{Sr} = ^{87}\text{Sr}/^{86}\text{Sr}_{\text{max}} - ^{87}\text{Sr}/^{86}\text{Sr}_{\text{min}}$  measured in the 50, 10, and 5 mg samples; Table 2 and Figure 1). Compared to previous isotopic determinations on the same samples at the RHUL and UV the new  $^{87}\text{Sr}/^{86}\text{Sr}$  data are more radiogenic reflecting the differences in the pretreatment procedure (different acid volume/sample amount). Aliquots of BEI reveal more radiogenic signatures ( $^{87}\text{Sr}/^{86}\text{Sr} = 0.723035\text{--}0.723107$ ), than NUS or JUD ( $0.719990\text{--}0.721614$ ). In marked contrast to the Sr isotopic compositions, the Nd isotopic signatures are apparently not significantly influenced by acid treatment as shown in Figure 1, where the new Nd isotopic data plot within  $\sim 1$   $\epsilon\text{Nd}$  unit compared to the previously measured ratios. At the same time, the various aliquots (50, 10, and 5 mg) of each sample display extremely homogeneous  $^{143}\text{Nd}/^{144}\text{Nd}$  isotopic signatures ( $\Delta^{143}\text{Nd}/^{144}\text{Nd} = 0.000008$  for BEI and  $0.000042$  for NUS, where  $\Delta^{143}\text{Nd}/^{144}\text{Nd} = ^{143}\text{Nd}/^{144}\text{Nd}_{\text{max}} - ^{143}\text{Nd}/^{144}\text{Nd}_{\text{min}}$  measured in the 50, 10, and 5 mg samples). Values of  $\epsilon\text{Nd}(0)$  of all three samples scatter around  $-10$ , with JUD being slightly less radiogenic (Table 2). While the different aliquots of BEI are dispersed in terms of  $^{176}\text{Hf}/^{177}\text{Hf}$  isotopic ratios, those of NUS show minor variabilities ( $\sim 1$   $\epsilon\text{Hf}$  unit; Figure 1). Both NUS and JUD have less radiogenic Hf isotopic compositions than BEI, with differences of ca 3–6  $\epsilon\text{Hf}$  units. Compared to previous Hf isotopic data of the three samples (BEI, NUS, JUD) acquired at RHUL, the newly determined Hf isotopic signatures are all less radiogenic by 1–3  $\epsilon\text{Hf}$  units (Table 2 and Figure 1).

#### 3.3. Modeling Results of Zircon Effects

MC simulations reveal that the Hf isotopic composition of the  $<10$   $\mu\text{m}$  size fraction of dust becomes less radiogenic (i.e., more negative  $\epsilon\text{Hf}(0)$  values) with increasing number of zircons present in the sample (Figure 2a). Hafnium carried by zircon grains may exceed 20 wt% of the total Hf amount in a sample (Figure 2b). At the same time, the  $^{176}\text{Hf}/^{177}\text{Hf}$  isotopic composition of the  $<2$   $\mu\text{m}$  fraction of dust is much less affected by zircons (Figure 2c) and the Hf hosted by these tiny (1–2  $\mu\text{m}$ ) zircon grains is usually in the range of 0.5 to 3 wt% compared to the total Hf content of a dust sample (Figure 2d). Sensitivity tests performed assuming zircons derived from Archean/Phanerozoic crust demonstrate that the  $\epsilon\text{Hf}(0)$  values of the  $<10$   $\mu\text{m}$  size fractions are influenced by the age and compositional range of zircon-bearing rocks present in the hinterland (supporting information Figures S3 and S4). By contrast, this influence is almost negligible for the  $<2$   $\mu\text{m}$  grain size fractions and their Hf isotopic compositions overlap with those of clays (and other heavy minerals having radiogenic Hf isotopic compositions) used in modeling ( $\epsilon\text{Hf}(0): 0.5 \pm 1.2$ ; supporting information Table S3).